Emerging Contaminants in Groundwater: 1,4-Dioxane and Poly- and Perfluoroalkyl **Substances (PFAS)**



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Arcadis June 8, 2016



Outline



- 1,4-Dioxane
 - Sources
 - Regulatory Status and Occurrence in Alabama Drinking Water
 - Fate and Transport
 - Site Characterization
 - Remediation Options
- Poly and Perfluoroalkyl Substances (PFAS)
 - PFAS Uses & History
 - Toxicology & Regulatory Evolution
 - PFAS in Alabama
 - PFAS Chemistry
 - Analytical Challenges & Advanced Analytical Solutions
 - Fate and Transport & Site Conceptual Model
 - Remediation Options



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1,4-Dioxane: Where it's Found

Consumer products

Detergents

Paint/
Dye/
Grease

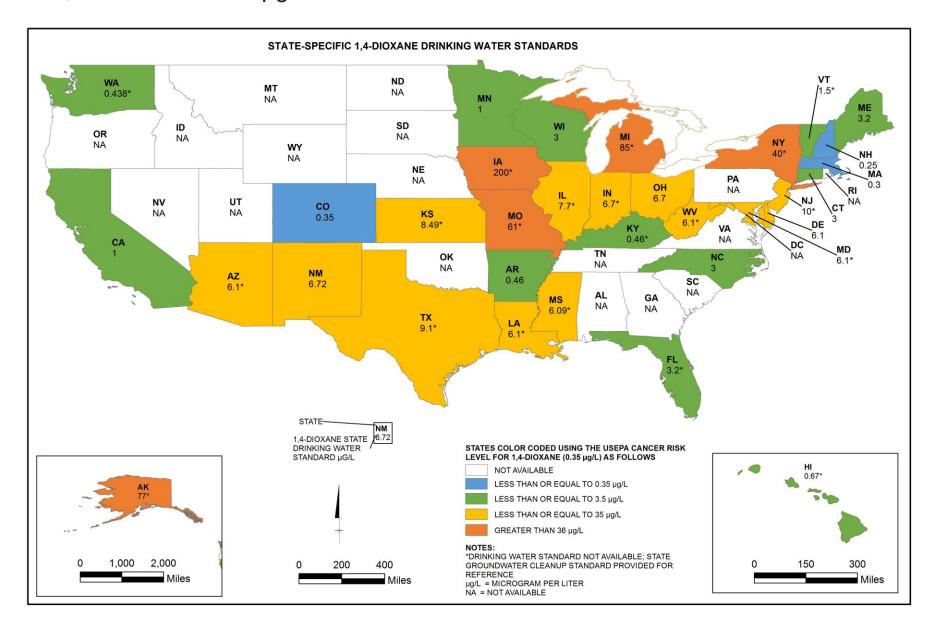
Manufacturing byproduct

Direct use

Chlorinated solvents (1,1,1-TCA)

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UCMR3 Detections of 1,4-Dioxane > 0.35 ppb (µg/L)

125 water utilities >1 ppb 1,4dioxane nationwide 4 are in Alabama

Greenhill Water

0.38 ppb 1,4-dioxane

Florence

0.93 ppb 1,4-dioxane

Sheffield

0.67 ppb 1,4-dioxane

Colbert County

1.0 ppb 1,4-dioxane

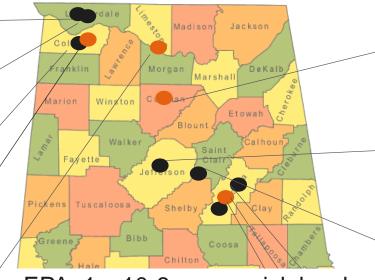
West Morgan East Lawrence

Decatur,

4.2 ppb 1,4-dioxane

Saraland,

0.5 ppb 1,4-dioxane



EPA: 1 x 10-6 cancer risk level for 1,4-dioxane is 0.35 µg/L



Vinemont,

2.5 ppb1,4-dioxane
Has switched water supply

Birmingham,

0.52 ppb1,4-dioxane

Leeds.

0.40 ppb1,4-dioxane

Talladega,

0.77 ppb 1,4-dioxane

Munford/Oxford Waterworks, 3.6 ppb 1,4-dioxane

Sylacauga,

0.36 ppb1,4-dioxane

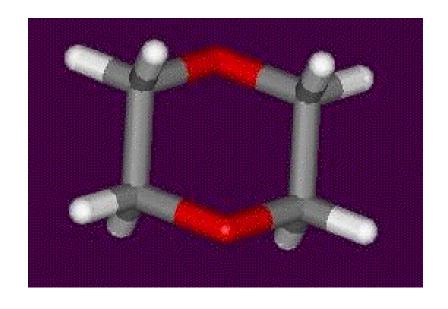
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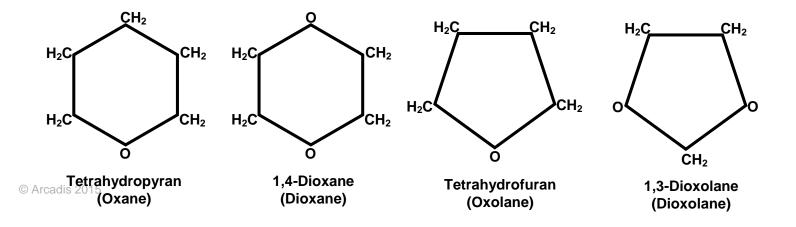


Fate and Transport

1,4-Dioxane Chemistry

- Highly soluble and stable in water
- Does not readily adsorb to organic material
- Can be stored by saturation of the static pore fraction

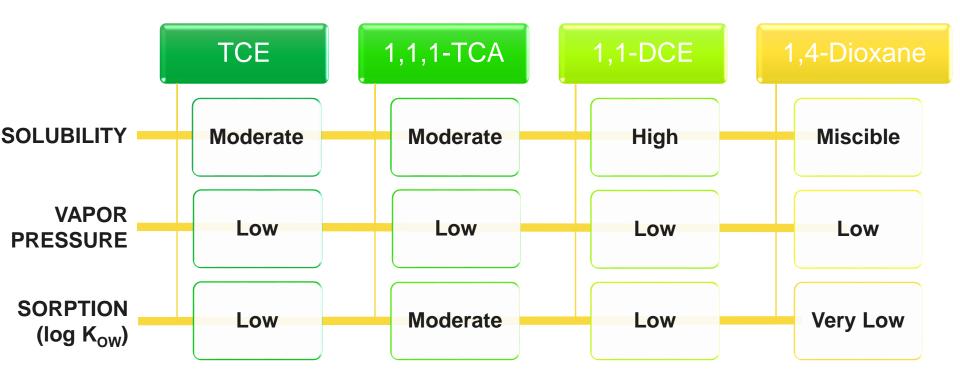






Fate and Transport

Comparison of parameters that dictate transport in groundwater for 1,4-dioxane and commonly known co-occurring contaminants

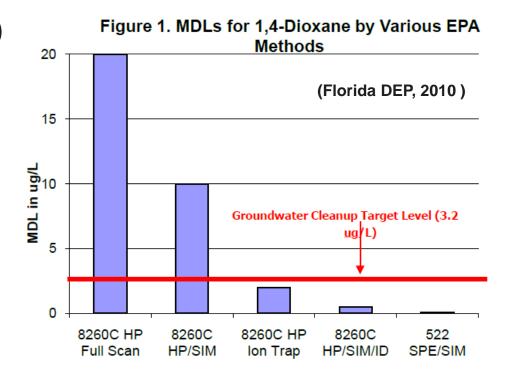


1,4-dioxane is expected to be more mobile in groundwater



1,4- Dioxane Analytical Methods

- EPA Methods (RL~ 1 μg/L)
 - 8260 with azeotropic distillation
 - 8260B SIM (Single Ion Monitoring)
 - 8260B SIM, isotope dilution
 - Modified 8270 with SIM, isotopic dilution
 - 522, drinking water method



- Specialized methods can achieve lower reporting limits
 - Columbia Analytical Lab uses solvent extraction, largevolume splitless injection to achieve RL ~0.1 µg/L



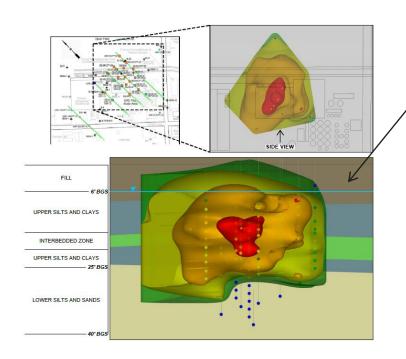
Site Characterization: Innovative Techniques

- Arcadis developed a partnership with TRIAD, a mobile laboratory contractor, to validate methods of rapid site characterization of cyclic ethers, including 1,4-Dioxane.
- Technique includes direct sampling ion trap mass spectrometer (DSITMS) using US EPA SW846 Method 8265 for the rapid on-site quantitative analysis of VOCs in groundwater, soil and vapor samples.
- The technology is capable of 2-3 minute quantitative analysis of soil and groundwater providing clients with up to 80 sample analysis per day, plus QC analyses.



High Resolution Site Characterization

DSITMS can also be used in conjunction with high resolution hydraulic conductivity measurement (such as Vertical Aquifer Profiling [VAP]) to determine potential presence of residual saturation separate phase and high level immobile dissolved phase contamination.



This high resolution 3-D model was created in real-time during the field effort to immediately evaluate all data and optimize field efforts!

Using the on-site laboratory instead of conventional off-site lab analysis resulted in approximately \$37,000 in savings!



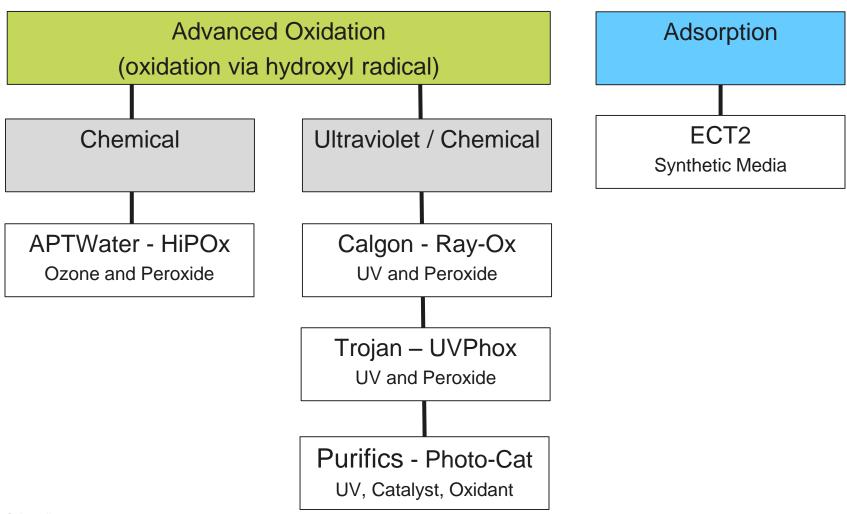
In-Situ Treatment Options

- In-Situ Chemical Oxidation (ISCO) using commonly used oxidants for groundwater remediation including persulfate, peroxide, permanganate, percarbonate, and O₃.
- Thermal treatment using ERH, TCH/IST, and SEE.
- In-situ biological treatment, primarily through co-metabolic pathways
- Monitored Natural Attenuation (MNA), dilution and mixing are likely to be the dominant mechanisms





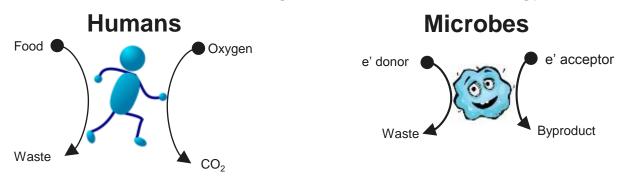
Ex-Situ Treatment Options



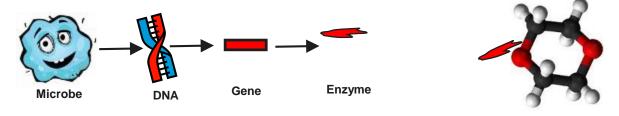


Metabolism vs. Co-Metabolism

Metabolism: the goal is to produce energy



Co-Metabolism: a fortuitous side reaction



Co-Metabolic Biodegradation ARCADIS Period Environment of the Consultance of the Consulta

Objective: Identify potential for cometabolic biodegradation mechanism

Locations selected for

- Presence of substrate (propane/methane)
- Presence of dissolved oxygen
- Spatial distribution

Approximate extent of VOCs in groundwater Approximate extent of 1,4-dioxane in groundwater Approximate extent of LNAPL

Approach:

- Deployed BioTrap® samplers in-well for 30 days
- Analyzed both DNA & RNA
- •Quantified propane and soluble methane monooxygenase genes



www.microbe.com

Monitored Natural Attenuation PARCADIS | Design & Consultancy for natural and built assets | Site Closure

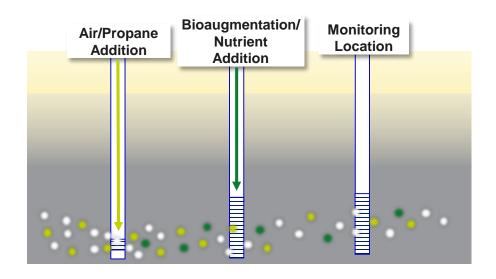




Propane Biosparge to Enhance Co-Metabolic Transformation

Active injection approach:

- ✓ Inject air and propane (gas injection)
- ✓ Inject bioaugmentation culture and nitrogen/phosphate nutrients (liquid injection)
- ✓ Monitor for biodegradation of 1,4-dioxane



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Line to Sparge

Well

Propane Sparge System

Propane

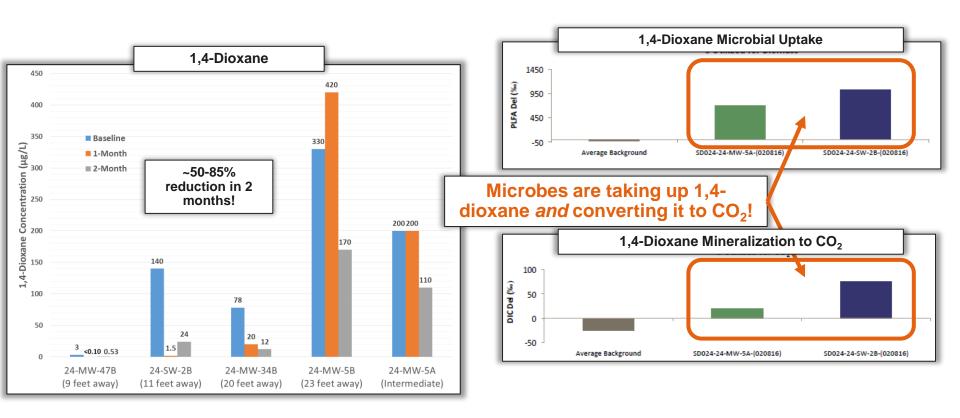
Tank



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Biosparge Pilot Results



SIP demonstrated biodegradation as mechanism for 1,4-dioxane reductions!

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1,4-Dioxane Summary



- Highly mobile & miscible in groundwater
- Regulatory standards vary by state
 - U.S. EPA: 1 x 10-6 cancer risk level for 1,4-dioxane in drinking water is 0.35 µg/L – not an MCL
- ISCO and thermal treatment work for confined source areas
- Ex situ treatment more appropriate for large plumes; variety of strategies available
 - GAC and air stripping do not work
- Co-metabolic biodegradation is possible MNA may be possible for some sites
- Arcadis is piloting propane sparging to enhance cometabolic biodegradation





Multiple and Varied PFAS Uses Examples of Common Uses:

- Consumer Products
 - Oil and water resistant finishes on paper, textiles, carpeting, cookware
- Aqueous film forming foams (firefighting)
- Electroplating mist suppressants
- Semiconductor manufacture
- Aerospace and electronics applications















Major Locations of PFAS Contamination

- Dept. of Defense Sites
- Refineries
- Large Rail Yards
- Chemical Facilities
- Commercial and private airports
- Municipal Fire Training Areas
- Landfills
- Fire Stations
- Plating Facilities
- Biosolids land application









PFAS Exposure, Distribution, and Elimination in Humans

EXPOSURE

DISTRIBUTION

ELIMINATION

- Most exposure is likely from ingestion of contaminated food or water
- Exposure also comes from:
 - Breast milk
 - Air
 - Dust (especially for children)
 - Skin contact with various consumer products

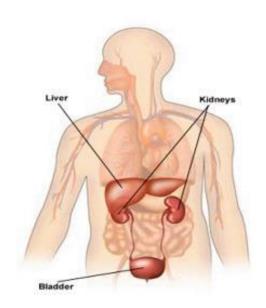
- PFAS bind to proteins, not to fats.
- Highest concentrations are found in blood, liver, kidneys, lung, spleen and bone marrow.
- PFOS and PFOA have bioaccumulative properties.
- Shorter chain PFAS generally have a lower bioaccumulation potential, although there may be some exceptions.

- Elimination of PFOS and PFOA from the human body takes some years, whereas elimination of shorter chain PFAS are in the range of days
- Apart from chain length, blood halflives of PFAS are also dependent on gender, PFAS-structure (branched vs. straight isomers), PFAS-type (sulfonates vs. carboxylates) and species.
- Elimination mainly by urine.



Toxicity

- Several human epidemiological studies show inconsistent results. Elevated levels of PFOS and PFOA are associated with increases in blood cholesterol and liver damage. It is however not clear, if these effects are caused by PFAS.
- Based on results of chronic studies with animals (mainly mice, rats and monkeys), there are concerns that PFOS and PFOA cause effects on the liver, lipid metabolism, immune response, reproduction and development.
 - Extrapolation from animals to humans is difficult, as humans and animals react differently to PFAS.
- The C8 Science Panel determined a probable link between high levels of PFOA exposure and kidney and testicular cancer, hypertension in pregnancy, ulcerative colitis, cholesterol, and thyroid disease
- Toxicity of PFAS other than PFOS and PFOA have not been well-characterized.



http://www.c8sciencepanel.org/



Target Regulatory PFAS Values

		Va	lues in pa	renthese	s refer to	PFAS red	gulated as	s a sum c	oncentrat	ion	_			
Drinking Water Crite	eria in µg/l i	n Europear	n Countries											
	PFOS	PFOA	PFOSA	PFBS	PFBA	PFPeA	PFHxA	PFHpA	PFNA	PFDA	6:2 FTS	PFHpS	PFHxS	PFPeS
Denmark	(0.1)	(0.1)	(0.1)	(0.1)	(0.1)	(0.1)	(0.1)	(0.1)	(0.1)	(0.1)	(0.1)	-	(0.1)	-
Germany	0.3	0.3	-	-	-	-	-	-	-	-	-	-	-	-
The Netherlands	0.53	-	-	-	-	-	-	-	-	-	-	-	-	-
Sweden	0.09	0.09	-	0.09	-	-	-	-	-	-	-	-	-	-
U.K.	0.3	0.3	-	-	-	-	-	-	-	-	-	-	-	-
Drinking Water Crite	eria in µg/l l	J.S.												
	PFOS	PFOA	PFOSA	PFBS	PFBA	PFPeA	PFHxA	PFHpA	PFNA	PFDA	6:2 FTS	PFHpS	PFHxS	PFPeS
Minnesota	0.3	0.3	-	7	7	-	-	-	-	-	-	-	-	-
New Jersey	-	0.04	-	-	-	-	-	-	0.013	-	-	-	-	-
Vermont		0.02												
U.S. EPA	(0.07)	(0.07)	-	-	-	-	-	-	-	-	-	-	-	-
Canada	0.3	0.7	-	-	-	-	-	-	-	-	-	-	-	-
Groundwater Criteri	a in µg/l in l	European (Countries											
	PFOS	PFOA	PFOSA	PFBS	PFBA	PFPeA	PFHxA	PFHpA	PFNA	PFDA	6:2 FTS	PFHpS	PFHxS	PFPeS
Denmark	(0.1)	(0.1)	(0.1)	(0.1)	(0.1)	(0.1)	(0.1)	(0.1)	(0.1)	(0.1)	(0.1)	-	(0.1)	-
Germany	-	-	-	-	-	-	-	-	-	-	-	-	-	-
State of Bavaria	0.23	-	-	3	7	3	1	0.3	0.3	0.3	-	-	-	-
State of Baden	0.23	0.3	-	3	7	3	1	0.3	0.3	0.3	0.3	0.3	0.3	1
Württemberg	0.23	0.3												
The Netherlands	0.023	-	-	-	-	-	-	-	-	-	-	-	-	-
Groundwater Criteri	a in µg/l in	U.S.												
	PFOS	PFOA	PFOSA	PFBS	PFBA	PFPeA	PFHxA	PFHpA	PFNA	PFDA	6:2 FTS	PFHpS	PFHxS	PFPeS
New Jersey	-	-	-	-	-	-	-	-	0.02	-	-	-	-	-
Texas, Residential	0.56	0.29	0.29	34	71	1.9	1.9	0.56	0.29	0.37	-	-	1.9	-
Soil Criteria in mg/k	g in Europe	an Countri	es, U.S.											
	PFOS	PFOA	PFOSA	PFBS	PFBA	PFPeA	PFHxA	PFHpA	PFNA	PFDA	6:2 FTS	PFHpS	PFHxS	PFPeS
Denmark	(0.4)	(0.4)	(0.4)	(0.4)	(0.4)	(0.4)	(0.4)	(0.4)	(0.4)	(0.4)	(0.4)	-	(0.4)	-
Germany	-	-	-	-	-	-	-	-	-	-	-	-	-	-
State of Bavaria		Evaluation for pathway Soil -> Groundwater is based on Leachate Concentrations (μg/l)												
	Evaluation for recycling of Soils is based on LAGA M20 Criteria													
The Netherlands	0.0032	-	-	-	-		-	-	-	-	-	-	-	-
Texas, Residential	1.5	0.6	0.058	73	150	5.1	5.1	1.5	0.76	0.96	-	-	4.8	-



Historical Perspective on PFAS



1938: Roy Plunkett discovers polytetrafluoroethylene (PTFE)

1954: Production of first PTFE-coated, non-stick cookware.





1968: U.S. Navy develops first PFAScontaining firefighting foams known as AFFF in response to catastrophic ship fires.



1997: PFOS ubiquitously detected in blood bank samples from non-occupationally exposed people around the world



2006: Eight major manufacturers commit to phase out PFOA by 2015 as part of U.S. EPA PFOA Stewardship Program



2013: After 7 years of research, C8 Science Panel determines probable link between PFOA exposure with ulcerative colitis, high cholesterol, pregnancy-induced hypertension, thyroid disease, and kidney and testicular cancer.

1949: Products containing PTFE first used for coatings of pipes and leak proofing of pipe connections.



1956: Products containing perfluorooctane sulfonic acid (PFOS) become a popular treatment for clothes, carpets, and furniture.

1978: Manufacturers become aware of C8 PFAS in blood of their manufacturing workers



2002: The primary global manufacturer of PFOS phases out PFOS production and related chemistries







2009: The Stockholm Convention classes PFOS as a Persistent Organic Pollutant and add it to Annex B to restrict it's use.



Recent Acceleration of Attention on PFAS

2015: Phase-out of PFOA completed by eight leading manufacturers as part of US EPA Stewardship Council.



May 2015: Hundreds of prominent scientists and professionals sign on to the Madrid Statement, urging a complete move away from PFAS chemistry.



The Madrid Statement on Poly- and Perfluoroalkyl Substances (PFASs)

http://dx.doi.org/10.1289/ehp.1509934

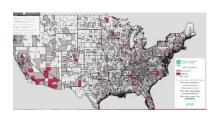
January 2016: Manufacturing facility in Hoosick Falls, NY named first PFAS-related Superfund site for PFOAcontaminated drinking water





June 2, 2016:. 100k Alabama residents advised not to drink their local drinking water

2015: U.S. EPA UCMR3 sampling of public drinking water finds PFAS in 97 public drinking water supplies.



October 2015: A manufacturer was found liable for a woman's kidney cancer in its first of 3500 personal lawsuits related to PFOA contamination of drinking water near a manufacturing facility in Parkersburg, WV.

February 2016: Guernsey, a Channel Island, loses lawsuit against a manufacturer in pursuit of costs related to cleanup of PFOS-contaminated groundwater and soil.



May 2016: US EPA announces drinking water health advisory limit for PFOS and PFOA (separately or combined) at 70 ppt (ng/L)



UCMR3 Detections of PFOS and PFOA > 70ppt (2016 USEPA Health Advisory)

PARCADIS Design & Consultancy for natural and built assets

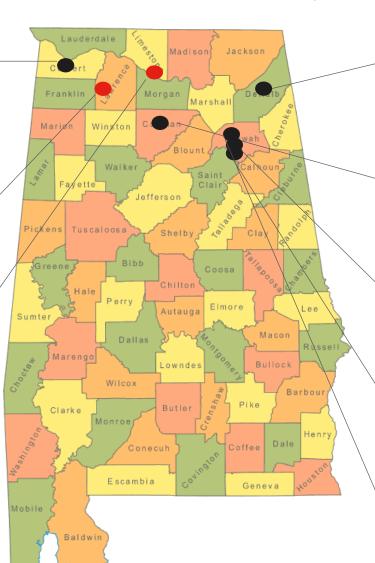
Colbert County
70 ppt PFOS + PFOA

West Lawrence Water Co-op Mt. Hope, 140 ppt PFOS + PFOA

West Morgan East Lawrence Decatur, 230 ppt PFOS + PFOA

60 Water Utilities >70 ppt Nationwide 8 were in Alabama

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Northeast Alabama Water Supply, Fort Payne, 111 ppt PFOS + PFOA Has switched water supply

Vinemont, 270 ppt PFOS + PFOA Has switched water supply

Gadsen,
90 ppt PFOS + PFOA
Monitoring water supply

Southside Water Works, 80 ppt PFOS + PFOA

Rainbow City, 100 ppt PFOS + PFOA

UCMR3 Detections of PFOS and PFOA > 70ppt (2016 USEPA Health Advisory)

PARCADIS Design & Consultancy for natural and built assets

West Lawrence Water Co-op Mt. Hope, 140 ppt PFOS + PFOA



West Morgan East Lawrence Decatur, 230 ppt PFOS + PFOA

State Advisory remains for only 2 water supplies





pubs.acs

2011

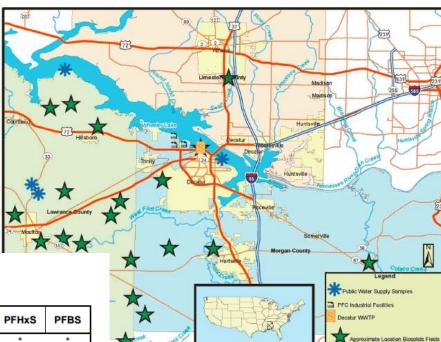
Application of WWTP Biosolids and Resulting Perfluorinated Compound Contamination of Surface and Well Water in Decatur, Alabama, USA

Andrew B. Lindstrom,*,† Mark J. Strynar,† Amy D. Delinsky,† Shoji F. Nakayama,[§] Larry McMillan,‡ E. Laurence Libelo,^{||} Michael Neill,[⊥] and Lee Thomas[⊥]

Table S6A. Perfluorinated compound concentrations in well water samples in ng/L

Sample Name	PFDA	PFNA	PFOA	PFHpA	PFHxA	PFPeA	PFBA	PFOS	PFHxS	PFBS
W06PW	*	*	*	*	*	*	*	*	*	*
W14PW B	*	25.7	594	619	570	333	180	14.1	20.7	25.4
W63PW	*	*	*	*	*	*	*	*	•	•
W07PW	*	*	*	*	9.72	*	45.8	*		•
W101PW	*	*	*	*	*	*	14.6	*	•	22.9
W58PW	*	*	*	*	*	*	*	*	*	*
W09SW	*	*	*	*	*	*	10.4	*	*	*
W02PW	*	*	*	*	*	*	*	*	*	*
W54PW β	*	*	2070	2100	2150	1180	680	*	46.4	56.5
W15PW	*	*	*	*	15.8	12.2	42.6	*	*	•
W62PW B	*	*	*	*	*	*	*	*	•	•
W22PW β	*	*	*	*	*	*	*	*		*
W11PW β	*	*					34.6	12.0	12.7	26.4
W60PW	*	*	149	77.2	150	57.2	98.1	151	56.5	33.9
W12PW	*		6410	5220	3970	2330	1260	*	87.5	76.6
W08PW	*	*	*	*	*	*	*	*	•	•
W01PW B	*	*	*	*	*	*	24.1	*		10.1
W17PW	*	*	*	*	*	*	13.2	*	*	
W19PW	*	*	*	*	*	*	11.6	*	•	•
Max =	*	25.7	6410.0	5220.0	3970.0	2330.0	1260.0	150.6	87.5	76.6
Min =	*	25.7	149.2	77.2	9.7	12.2	10.4	12.0	12.7	10.1

^{*} Values below the limit of quantitation (LOQ)



l applications of biosolids from the Decatur Utilities Dry Creek Waste Water Treatment Plan

[†]U.S. Environmental Protection Agency, National Exposure Research Laboratory, Research Triangle Park, North Carolina 277 United States

^{*}National Caucus & Center on Black Aged, Inc., Durham, North Carolina, United States

⁵U.S. Environmental Protection Agency, National Risk Management Research Laboratory, Cincinnati, Ohio 45268, United Sta

U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxics, Washington, DC 20460, United States

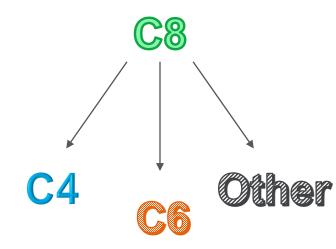
¹U.S. Environmental Protection Agency Region IV, Atlanta, Georgia, United States

β indicates sample from a well used for drinking water



PFAS Manufacturing: Beyond PFOS and PFOA

- In most of the U.S. and Europe, C8 PFAS species have been phased-out due to potential health concerns
- PFOS (C8) and PFOA (C8) and related PFAS have been replaced with compounds with shorter (e.g., C4, C6) perfluorinated chains
- Shorter chain replacement chemicals are typically less bioaccumulative, but they are still persistent and more mobile in aqueous systems.
- Solutions for characterizing all PFAS species, from C4 to C8, are imperative; all carbon chain lengths are present in most environmental samples and even in historical "C8" products



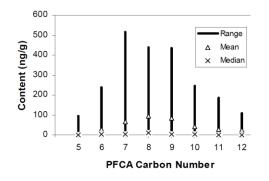


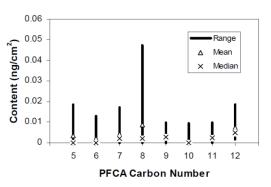
Perfluorinated carboxylates in consumer products

2007-2008

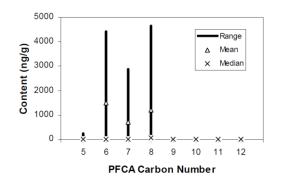
 Focus has mainly been on PFOA and PFOS, but PFAS-containing products typically contain a mixture of species in a single product

- C5 to C12 perfluorinated carboxylates are present in many PFOA (C8)-containing consumer products
- Similar diversity of PFAS chain lengths, as well as structures, may be expected in other PFAScontaining products and PFAScontaminated areas.



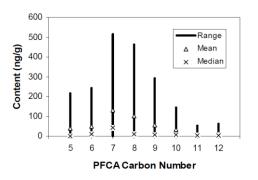


Treated Home Textiles



Food contact paper

Non-stick cookware

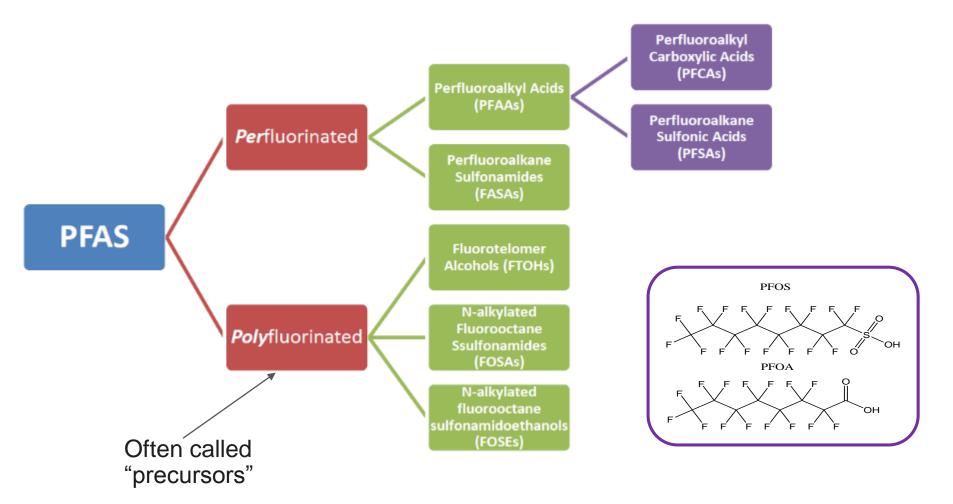


Pre-Treated Carpet

Data from Guo et al. 2009, U.S. EPA; Polyfluorinated substances and perfluorinated sulfonates were not measured



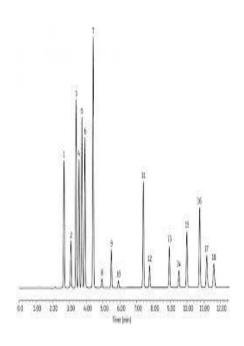
PFAS Classes: Per- vs. Poly-





Analytical Challenges

- PFAS is a class of thousands of compounds
- Current analytical methods only examine a small fraction of the compounds present (16 - 39 compounds); US EPA 537 includes 12 species
- It is not possible to measure each chemical individually



Advanced Analytical Techniques:



LC-MS/MS

- Most common tool is LC-MS/MS US EPA Method 537
- Can detect C4 to C12 perfluorinated carboxylates (PFCAs) & sulfonates (PFSAs)
- Detection limits to approx. 0.09 ng/L

Total Oxidizable Precursors (TOP) Assay

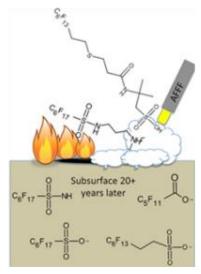
- Pre-treatment of samples using conventional chemical oxidation which converts precursors to perfluorinated carboxylates (PFCAs) that can be detected by LC-MS/MS
- Detection limits similar to LC-MS/MS to approx. 2 ng/L

Particle Induced Gamma Emission (PIGE) and Adsorbable Organic Fluorine (AOF)

- Both measure Total Organic Fluorine
- Detection Limits > 1000 ng/L

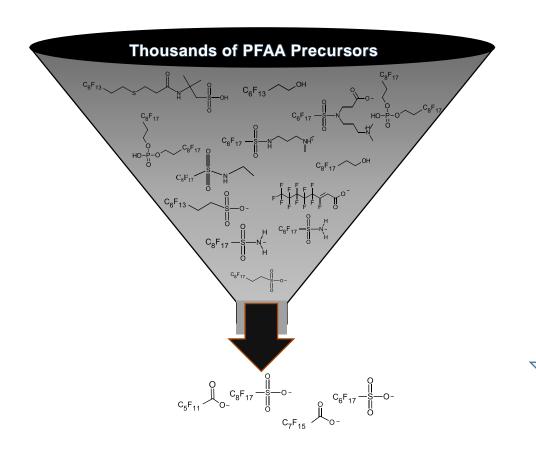








Aerobic Biotransformation Funnel



All Polyfluorinated / PFAA Precursor Compounds in Commerce ("Dark Matter")

Hundreds of Common Intermediate Transformation Products

Approximately 25 PFSAs, PFCAs, PFPAs –collectively termed PFAA's

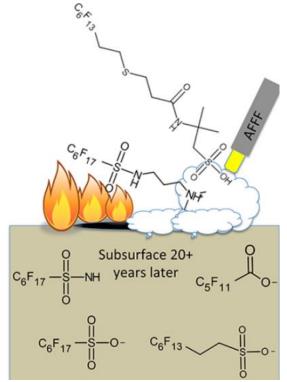
PFAS do not biodegrade – i.e. mineralize, they biotransform and many parent or intermediate compounds are not detected by conventional analytical methods



Digest precursors and measure the hidden mass: TOP Assay

- This analytical method converts PFAA precursors to PFAAs
- Termed Total Oxidizable Precursor (TOP) Assay
- PFAAs measured before and after TOP Assay

 increase is equivalent to the precursor
 concentration in the sample



Persistence of Perfluoroalkyl Acid Precursors in AFFF-Impacted Groundwater and Soil

Erika F. Houtz, Christopher P. Higgins, Jennifer A. Field, and David L. Sedlak,

Conventional analytical tools fail to measure the hidden PFAS precursor mass, the TOP assay solves this



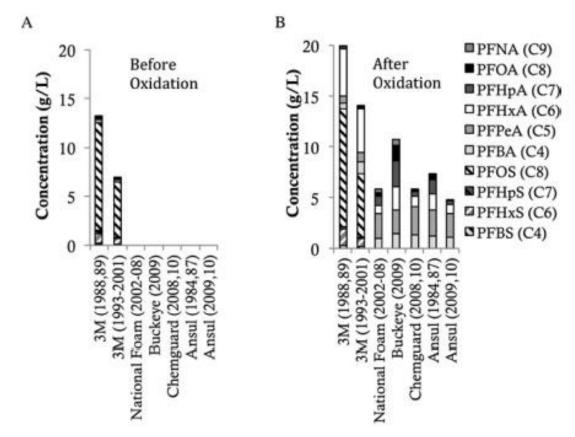


Figure 1. Average concentrations of perfluorinated sulfonates and carboxylates in AFFF formulations analyzed before (a) and after oxidation (b). Dates represent the years of manufacture of AFFF formulations analyzed in each category.

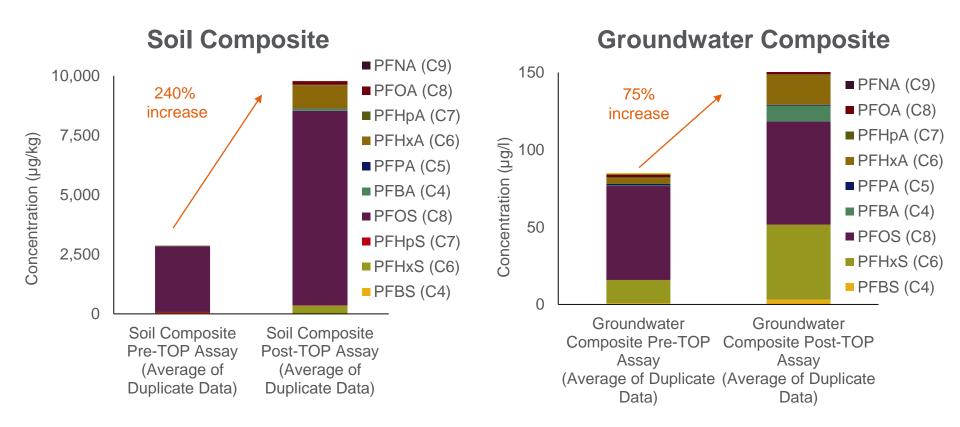
Persistence of Perfluoroalkyl Acid 1

Persistence of Perfluoroalkyl Acid Precursors in AFFF-Impacted Groundwater and Soil

Erika F. Houtz,[†] Christopher P. Higgins,[‡] Jennifer A. Field,[§] and David L. Sedlak[†],*



Total Oxidizable Precursor (TOP) Assay



- Significant increases in perfluorinated carboxylic acids and sulfonic acids (PFAAs) following TOP assay reveal the hidden mass of PFAA precursors present
 - An additional 240% of PFAS in soils and 75% in groundwater
- Demonstrates matrices impacted with AFFF contain a greater mass of PFAS than identified by conventional analysis with LC-MS/MS (EPA Method 537).



Fate and Transport: Polyfluorinated Substances/ Precursors

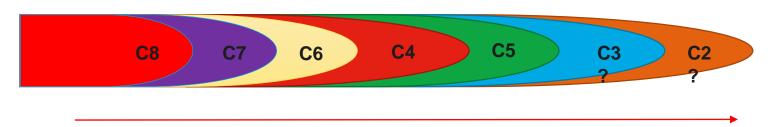
- Physicochemical properties vary
 - Some are very mobile in groundwater, some are not
 - Some are volatile, some are not
- Can biotransform to perfluorinated substances
- Can readily react with hydroxyl radical and other abiotic species to form perfluorinated substances
- None can completely biodegrade to benign products





Fate and Transport: Perfluorinated Substances

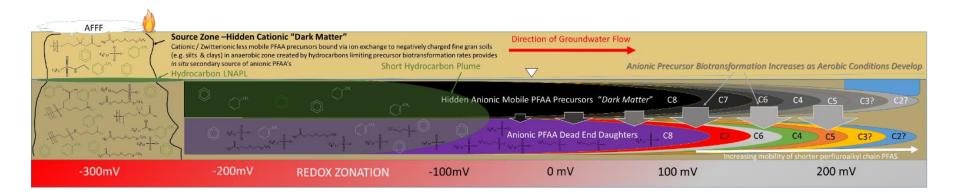
- Typically negatively charged at environmental pH
- Non-volatile
- Mobile in groundwater; mobility decreases with increasing perfluorinated chain length
- Cannot biotransform or biodegrade
- Cannot react with typical oxidants and reductants



Direction of Groundwater Flow



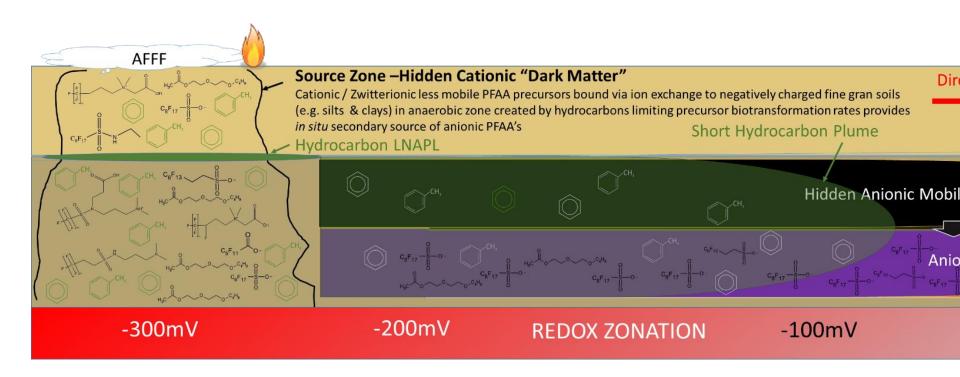
Conceptual Site Model



- Source zone hidden cationic & cation dominated zwitterion "Dark Matter" in more anaerobic environment
- Mobile zone hidden anionic & anion dominated zwitterions (more mobile)
 PFAA precursors, "Dark Matter"
- Anionic precursor biotransformation increases as aerobic conditions develop in the downgradient of hydrocarbon plume
- Increasing mobility of shorter perfluoroalkyl chain PFAS

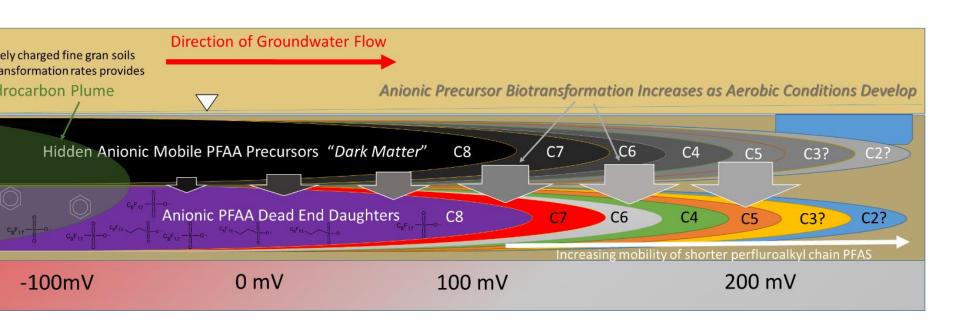


Source Zone -CSM



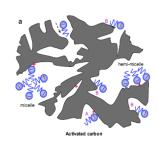


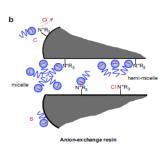
Plume -CSM





PFAS Groundwater Remediation





- Currently proven commercial option is pump and treat for PFOS and PFOA
 - GAC can be effective in removing PFOS/PFOA, however sorption is low and competition occurs (much higher costs than for conventional contaminants)
 - GAC increasingly less effective as PFAS chain length decreases
 - Ion exchange resins or polymers with a large surface area may be suitable for low concentrations and high volumes
 - Other potential techniques are nanofiltration and RO
- Oxidation via conventional methods is difficult due to strength of the C-F bond and may lead to higher PFCA / PFSA levels as a result of precursor breakdown using oxidants
- Arcadis ScisoR shown to defluorinate PFOS with in situ treatment planned for 2016

P&T with GAC treatment is the most commonly applied technology –less effective on shorter chain PFAS



Cost of PFOS Groundwater Treatment with GAC

- Low sorption of PFAS → higher GAC consumption, cost
- At influent concentrations 3 to 20 μg/L; effluent 0.1 μg/L

Parameter	Charge capacity	Annual GAC Costs (\$/Year)			
	(% wt)	75 Lpm	166 Lpm	832 Lpm	1,665 Lpm
PFOS	0.002 to 0.005	3,932	7,865	39,322	78,643
Chlorinated hydrocarbons	0.02 to 0.4	256	512	2,555	5,112
BTEX	0.1 to 2.0	52	102	512	1,022
PAH	1.3 to 2.5	29	57	284	568



PFAS Soil Remediation

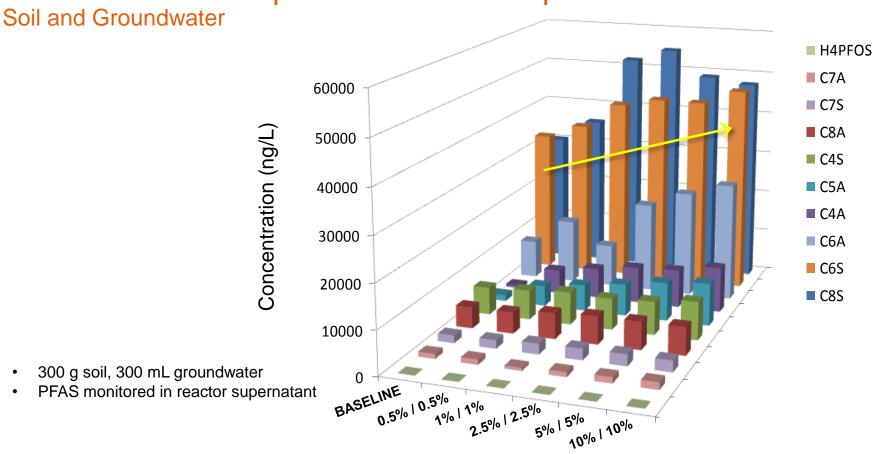


- Currently options are limited to excavation, stabilization or capping
- Landfilling introduces challenges since PFAS will become constituents of leachate (landfill leachate is not typically being evaluated for e.g. PFOS)
- Incineration, high temperatures (> 1,100 °C) are needed to cleave the stable C-F-bonds
- Immobilization with GAC or commercial products (soil mixing) e.g. Rembind.
- Solidification (e.g. cement) is a yet unproven long-term option
- Arcadis ScisoR trials on soil mixing progressing

Soil remediation largely relies on excavation/stabilization/ immobilization and not destruction



Oxidation Results: peroxide activated persulfate

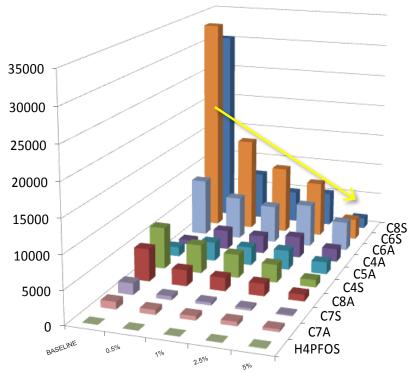


Conventional ISCO creates PFAAs from precursors



Oxidation Results: ScisoR®

Soil and Groundwater



- Destruction of PFAS and PFAA's in soil and groundwater by chemical oxidation / reduction using ScisoR[®]
- Effective at ambient temperature
- Reagents can be injected or mixed with impacted soil and groundwater
- In Situ remediation of PFAS impacted source areas enabled
- Could be used to regenerate sorbent media (e.g. GAC, ion exchange resins)
- Patent granted in NL. Provisional patent in the US. Patent Cooperation Treaty (PCT) procedure pending for worldwide patent rights

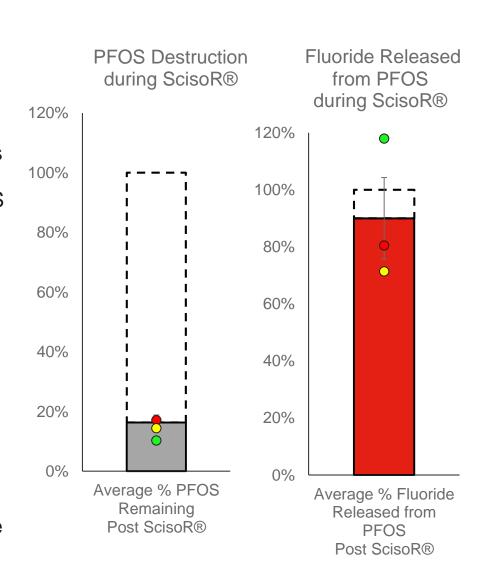
- 300 g soil, 300 mL groundwater
- PFAS monitored in reactor supernatant

ScisoR destroys PFAAs and precursors

PFAS Remediation: ScisoR



- 10 mg/L PFOS starting concentration
- 3 replicate data sets
- 83 to 90% PFOS destruction after 14 days
- 71% to 118% fluoride released from PFOS during SCISOR
- Overall fluoride mass balance (remaining fluoride in PFOS + fluoride released to solution)
 - 86% to 126% of theoretical
- All treated samples were blind spiked with 10 mg/L fluoride
 - 80% to 99% spike recovery
- Longer reaction times and repeat applications of ScisoR will cause complete destruction of PFOS





ScisoR Field Demonstrators

- ScisoR Ex Situ On Site Remediation of Unsaturated Soils
- ScisoR In Situ Aquifer Remediation
- 1. Laphroaig Europe, June 2016 site work
- 2. **Port Ellen** UK, April 2016 lab
- 3. **Gartbreck** North America 2016 repeat lab with TOP
- 4. Bowmore Australia, May 2016 lab





PFAS Summary



- Many uses firefighting foams are a major source in groundwater
- New EPA Health Advisories (70 ppt PFOS + PFOA) impact Alabama drinking water
- PFAS are a class of many compounds with varying properties, but none can completely biodegrade
- Precursor compounds are often present that biotransform to make more PFOS, PFOA, and similar perfluorinated acids
- Arcadis is focusing on commercializing more advanced PFAS characterization tools
- Existing groundwater treatment options are pump and treat with GAC or membranes
- Arcadis has developed an in situ remedy for PFAS destruction that we are imminently testing at firefighting sites – called ScisoR



Thank you

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Arcadis authored CONCAWE PFAS guidance soon to be published